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(56) Documents cited

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(54) Modified tin brightener for tin-zinc alloy electroplating bath

(57) The brightener comprises an aqueous solution containing acetaldehyde and formaldehyde as primary brightener, an alcohol such as n-propyl alcohol, a surfactant and one component of a conventional two-part tin brightener as a secondary brightener. The modified brightener is suitable for use as a brightener in the deposition of tin-zinc alloys. The function of the other component of the tin brightener is accomplished by the formaldehyde and acetaldehyde. The problem of imbalance of the two components which can adversely affect brightening is thereby avoided. The tin brightener component may be a mixture of methanol, glycolated ethylene oxide, sulphuric acid, potassium acid tartrate, butyrophene, zinc sulphate and hydroxylamine sulphate. The composition may also include allylacetate as a preservative and additional stabilizing agents.

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TIN-ZINC ALLOY BRIGHTENERBACKGROUND OF THE INVENTIONFIELD OF THE INVENTION

This invention relates generally to the field of electroplating alloys of tin and zinc, and specifically to a brightener for use in a tin-zinc plating bath.

BACKGROUND ART

Brighteners are widely used in electroplating processes to provide a pleasing decorative finish to the electrodeposited metal. In particular, there are numerous commercially available brighteners for use in conventional tin plating processes. However, such brighteners do not affect the brightness of zinc, and thus their use with a tin-zinc alloy will result in a deposit having a mottled granular appearance.

The present invention provides an aqueous brightener for the electrodeposition of tin-zinc alloys and one that is particularly useful in a sulfuric acid-based plating solution.

#### SUMMARY OF THE INVENTION

The brightener of the present invention comprises an aqueous solution of acetaldehyde, formaldehyde, an alcohol such as n-propyl alcohol, a surfactant and one component of a conventional tin brightener. The composition may also include allylacetoacetate as a preservative and additional stabilizing agents.

## DETAILED DESCRIPTION OF THE INVENTION

In the following description, for purposes of explanation and not limitation, specific substances, concentrations, etc. are set forth in order to provide a thorough understanding of the present invention. However, it will be apparent to one skilled in the art that the present invention may be practiced in other embodiments that depart from these specific details. In other instances, detailed descriptions of well known processes are omitted so as to not obscure the description of the present invention with unnecessary detail.

The preferred brightener composition contains (1) acetaldehyde, (2) formaldehyde, (3) alcohol, (4) a surfactant and (5) a tin brightener. Although not essential, the brightener preferably further includes allylacetoacetate and a stabilizing agent.

The relative concentrations of the constituent chemicals are set forth in Table 1 below, the balance of the composition comprising distilled or deionized water. Minimum, nominal and maximum values are given for the concentrations of each constituent. The nominal values are consistent with experimental results, and are known to provide satisfactory performance. It is believed that comparable performance may be achieved with concentrations anywhere within the indicated ranges or even beyond. Thus, this invention is not strictly limited to the values given.

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CONSTITUENT	CONCENTRATION (per liter)		
	MINIMUM	NOMINAL	MAXIMUM
acetaldehyde	2 ml	30 ml	150 ml
formaldehyde	5 ml	80 ml	250 ml
alcohol	2 ml	30 ml	150 ml
surfactant	1 ml	30 ml	150 ml
tin brightener	50 ml	350 ml	700 ml
allylaceto- acetate	5 g	50 g	200 g
stabilizer	per supplier's specifications		

n-propyl alcohol is suitable for use as the alcohol in the composition, however, any other common alcohol may be substituted therefor.

The surfactant of the preferred composition is "Triton X-100". "Triton X-100" is a trademark of Rohm & Haas Company designating a surfactant based on alkylaryl polyether alcohols, sulfonates and sulfates.

The acetaldehyde and formaldehyde act as a primary brightener for the tin-zinc deposit, breaking the granular structure throughout a current density range of approximately 1-100 ASF. Any conventional tin brightener may be used as a secondary brightener component, giving a lustrous plated appearance to the tin-zinc deposit. Only one component of a conventional two part tin brightener is used in the subject composition, the function of

the other component being accomplished by the addition of formaldehyde and acetaldehyde. This avoids a problem frequently encountered with the use of conventional two-part tin brighteners, whereby an imbalance of the two components may adversely affect the brightening of the deposit or may stop the plating process altogether.

A typical tin brightener suitable for use with the present invention is a composition of methanol, glycolated ethylene oxide, sulfuric acid, potassium acid tartrate, butyrophenone, zinc sulfate, and hydroxylamine sulfate. The potassium acid tartrate acts as a primary brightener and the methanol improves wetability. Glycolated ethylene oxide, a non-ionic surfactant and wetting agent, also assists as a secondary component of the brightener system. The zinc sulfate is used as a catalyst and the butyrophenone as an anti-oxidant to the chelating agents. The sulfuric acid is a pH adjuster, and the hydroxylamine sulfate is the oxygen scavenger for the brightener system preventing age discoloration.

Allylacetoacetate is preferably added to the composition as indicated in Table 1. Although not essential, this chemical acts as a preservative to extend the shelf-life of the brightener composition. Furthermore, most conventional tin brighteners contain benzolodene acetone, and allylacetoacetate assists in keeping this chemical in solution. In addition, allylacetoacetate is, by nature, a cleaning agent and assists in improving adhesion of the deposited alloy.

A stabilizing agent or antioxidant is preferably added to the composition to prevent the brightener from aging and/or discoloring. Any one of the following or similar chemicals may be added as the stabilizing agent: butyl hydroxytoluene (BHT), sodium benzoate, sodium erythorbate, hydroquinone and p-hydroxybenzoic acid ester. Of these, hydroquinone is also a reducing agent and will act as an additional brightening component.

The brightener of the present invention is preferably prepared by combining the acetaldehyde, formaldehyde and alcohol with an appropriate amount of distilled or deionized water while stirring continuously. The surfactant and allylacetoacetate are then added to the solution, followed by the selected tin brightener and stabilizing agent, while continuing to stir the mixture. The brightener as thus prepared has a shelf-life in the range of approximately 6 months to 1 year.

The brightener of the present invention is useful for a wide range of tin-zinc alloys ranging from approximately 98% tin-2% zinc which is widely used for electrical applications to approximately 75% tin-25% zinc which offers a high degree of corrosion resistance.

It will be recognized that the above described invention may be embodied in other specific forms without departing from the spirit or essential characteristics of the disclosure. Thus it

is understood that the invention is not to be limited by the foregoing illustrative examples except as set forth in the claims.



## CLAIMS

1. An aqueous brightener for the electrodeposition of tin-zinc alloy comprising:

- (a) approximately 2-150 ml/l acetaldehyde;
- (b) approximately 5-250 ml/l formaldehyde;
- (c) approximately 2-150 ml/l alcohol;
- (d) approximately 1-150 ml/l surfactant;
- (e) approximately 50-700 ml/l tin brightener.

2. The composition of claim 1 further comprising approximately 5-200 g/l allylacetoacetate.

3. The composition of claim 2 further comprising a stabilizing agent selected from the group consisting of butyl hydroxytoluene, sodium benzoate, sodium erythorbate, hydroquinone and p-hydroxybenzoic acid ester.

4. The composition of claim 1 wherein the alcohol is n-propyl alcohol.

5. An aqueous brightener for the electrodeposition of tin-zinc alloy comprising:

- (a) approximately 30 ml/l acetaldehyde;
- (b) approximately 80 ml/l formaldehyde;
- (c) approximately 30 ml/l alcohol;
- (d) approximately 30 ml/l surfactant;
- (e) approximately 350 ml/l tin brightener.

6. The composition of claim 5 further comprising approximately 50 g/l allylacetoacetate.

7. The composition of claim 6 further comprising a stabilizing agent selected from the group consisting of butyl hydroxytoluene, sodium benzoate, sodium erythorbate, hydroquinone and p-hydroxybenzoic acid ester.

8. The composition of claim 5 wherein the alcohol is n-propyl alcohol.

9. An aqueous brightener for the electrodeposition of tin-zinc alloy substantially as hereinbefore described.

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Examiner's report to the Comptroller under  
Section 17 (The Search Report)

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Relevant Technical fields

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(ii) Int Cl (Edition 5) C25D; C23C

Search Examiner

M J INSLEY

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

Documents considered relevant following a search in respect of claims

1-9

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2064585 A (ENTHONE) See Claim 1	1, 5 at least
Y	US 4428803 A (OMI) Whole document	1, 5 at least
Y	JP 020019490 (SHOWA ALUMINIUM) See Derwent Abstract number 90-064711/09	1, 5 at least
X Y	JP 510079643 (TOKYO SHIBAURA) See Derwent Abstract number 76-65509X/35	1, 5 at least

Category	Identity of document and relevant passages	Relevant to claim(s)

### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

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**A:** Document indicating technological background and/or state of the art.

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**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

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